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The dipole moment of formic acid

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With 2 figures in the text

The dipole moment of the monomeric formic acid molecule has been investigated previously by Zahn [1] and by Coop *et al.* [2]. In both cases the moment was obtained from the electric polarization of the vapour. In the present investigation the dipole moment has been determined from the Stark-effect splittings of some microwave rotational transitions. The result shows a considerable improvement in the accuracy of the total moment and gives also the orientation of the moment with respect to the inertia frame. Our results are $\mu = 1.35 \pm 0.02$ Debye units for the total moment and $\mu_a = 1.33 \pm 0.01$, $\mu_b = 0.21 \pm 0.07$ for the components. The results are in substantial agreement with the results $\mu = 1.52$ and $\mu = 1.4$ obtained in [1] and [2].

Experimental

The spectrometer used is essentially the same as the one described in [3]. Its frequency region has, however, been extended upward to about 50 kMHz by a very simple frequency doubler. This consists of a straight section of K-band waveguide provided with a receptacle for a 1N26 crystal cartridge. A probe from the central conductor of the cartridge protrudes into the electric field of the guide. Tuning of the multiplier is accomplished by choosing a suitable probe length and by varying the position of the cartridge. A filter section is placed in front of the detector cutting off the fundamental and passing only the harmonics. The rest of the equipment is identical with the K-band set-up. An oscilloscope display of one of the lines obtained in this way is shown in Fig. 1.

The field strength in the cell for different voltages applied was calibrated by measurements on some methyl alcohol lines. The results were in good agreement with the known dimensions of the cell and the assumption of an approximately homogeneous field.

Evaluation of the dipole moment

Since the molecule is known to be planar, the dipole moment should have components only in the directions of the a- and b-axes. The rotational lines, which are readily observed in the microwave region, are due to the a-component of the dipole. Some weaker lines due to the b-component have, however, been observed (C. Hearns, private communication). The present investigation involves a few μ_a-lines and one μ_b-line.

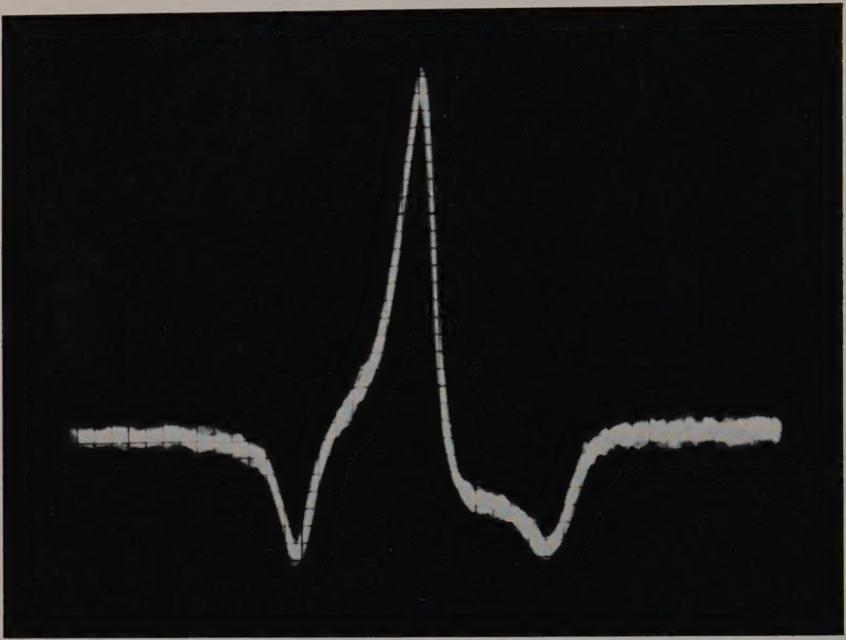

Fig. 1. The transition 1_{01}–2_{02} with the two Stark-effect components directed downward. Frequency increasing from left to right.

Following Golden and Wilson [4] the Stark-effect splittings of the lines may be expressed in the form

$$\Delta \nu = \frac{2E^2}{A+C}[\mu_a^2(\alpha_a + \beta_a M^2) + \mu_b^2(\alpha_b + \beta_b M^2)], \tag{1}$$

where E represents the electric field strength, A and C are rotational constants, while α_i and β_i are quantities dependent on the particular transition and the direction cosine matrix. The latter constants may be evaluated from tabulated values of line-strengths. Such tables with 0.1 intervals in $\varkappa$ have been calculated by Schwendeman and Laurie and were used in the present work with linear interpolation for the actual $\varkappa$-value. (The authors are obliged to Professor E. B. Wilson, Jr., for sending a copy of these tables.)

Inserting values of α and β for the various components measured, together with a value of $A+C$ from [5] equation (1) gives a set of relations between μ_a^2 and μ_b^2. These were plotted in a diagram and a fairly well determined point of intersection was obtained. The appearance of the diagram is shown in Fig. 2, where three components from different lines are represented. The average errors obtained in several measurements are also indicated. Intersections of lines representing the other components observed fall within the shaded area in the diagram. The resulting values obtained in this way are

$$\mu_a = 1.33 \pm 0.01 \text{ Debye units}$$
$$\mu_b = 0.21 \pm 0.07 \text{ Debye units}$$

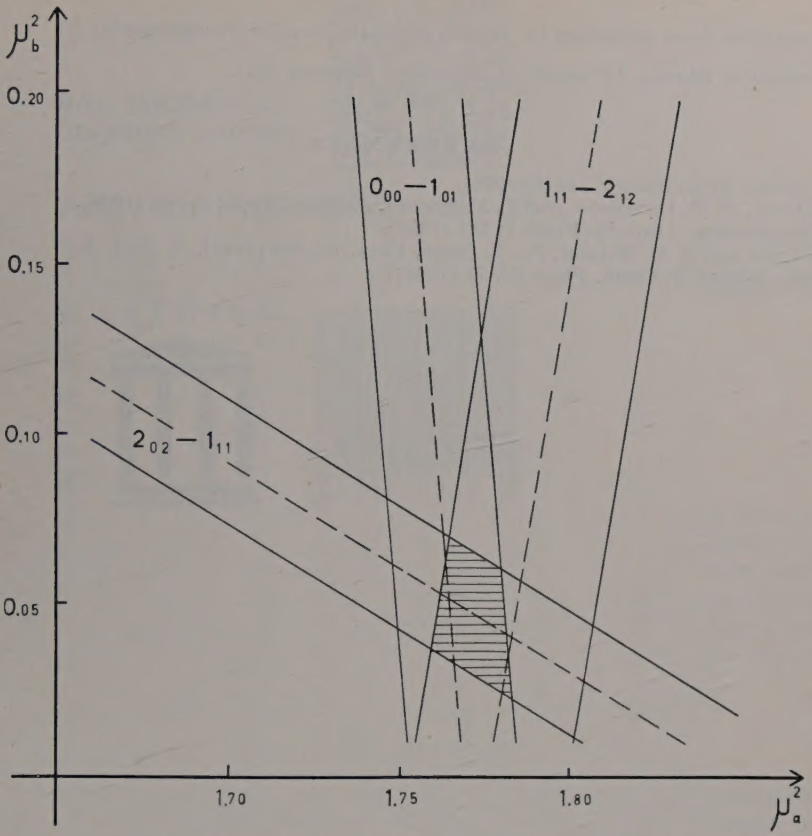

Fig. 2. Relations between μ_a^2 and μ_b^2 obtained from measurements of the Stark-effect of some lines.

If maximum observed errors are used rather than average errors the results become $\mu_a = 1.33 \pm 0.02$ and $|\mu_b| \leqslant 0.36$. The latter case does not exclude $\mu_b = 0$ but the intensity of the observed μ_b-line is in reasonable agreement with $\mu_b = 0.2$.

Experimental results on individual line components are given in Table 1.

Table 1.

Transition	M	$\Delta\nu/E^2$ (¹)
0_{00}–1_{01}	0	0.957 ± 0.009
2_{02}–1_{11}	0	-0.285 ± 0.005
1_{01}–2_{02}	0	-0.279 ± 0.004
	1	0.229 ± 0.003
1_{11}–2_{12}	1	6.10 ± 0.06
1_{10}–2_{11}	1	-5.65 ± 0.10

(¹) $\Delta\nu$ measured in MHz and E in e.s.u.

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